J|A|C|S COMMUNICATIONS

Published on Web 09/28/2009

Supramolecular Solar Cells: Surface Modification of Nanocrytalline TiO_2 with Coordinating Ligands To Immobilize Sensitizers and Dyads via Metal−Ligand Coordination for Enhanced Photocurrent Generation

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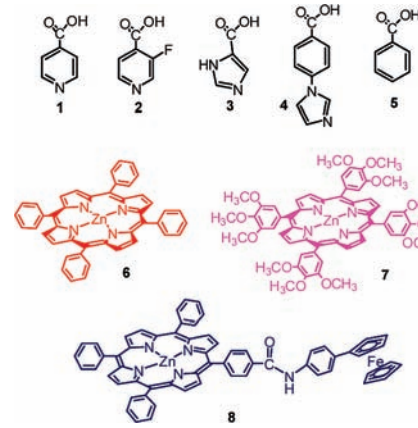
In nature, self-assembly through noncovalent binding motifs,[1a] such as hydrogen bonding, metal−ligand coordination, and electrostatic, $\pi-\pi$, and weak van der Waals interactions, plays a dominant role. For example, photosynthetic antenna reaction center pigments use such intermolecular forces to precisely arrange the donor−acceptor entities in a protein matrix, exhibiting a cascade of vectorial energy and electron transfer processes.[1b,c] Inspired by this revelation, several groups have constructed supramolecular photosynthetic architectures to mimic the photoinduced energy and electron transfer processes, with an ultimate goal of building efficient light-energy-harvesting devices based on these biomimetic principles.[2,3] Solar cells based on biomimetic principles could serve as an alternative to semiconductor-based ones for renewable energy production. Here, the design and construction of electron- and hole-transporting nanostructured architectures are pivotal for enhancing both charge separation efficiency and charge carrier mobility to improve the photovoltaic response.[3] Although donor−acceptor-type dyads have frequently been utilized for this purpose,[2] examples employing noncovalent methodologies, especially the highly versatile metal−ligand binding approach[4] for assembling the different entities on the electrode surface, have been scarce.[5]

Here we report a metal−ligand axial coordination approach[4] for the assembly of zinc tetrapyrrole sensitizers as well as a $(donor)_1-(donor)_2$ type dyad instead of the frequently used donor−acceptor-type dyads[2] on semiconducting TiO_2 surfaces. As demonstrated here, the present approach not only allows testing of the photoelectrochemical behavior of different zinc tetrapyrroles but also enables us to utilize fairly complex structures involving more than one donor entity. Additionally, utilization of the dyad markedly improves the current−voltage ($I-V$) performance of the photoelectrochemical cell through an electron transfer−hole migration mechanism.

In a typical experiment, a thin noncrystalline TiO_2 film-coated F-doped tin oxide (FTO) electrode (∼10−12 μm, tec7 from Pilkington) was surface-modified with an axially coordinating ligand bearing a carboxylic acid (compounds **1**−**5** in Chart 1) by placing the electrode in an ethanolic solution of the desired compound overnight. After removal of the unbound molecules (two or three ethanol washings), the TiO_2 electrode was immersed in an *o*-dichlorobenzene (DCB) solution containing the desired zinc tetrapyrrole (**6**−**8** in Chart 1) for 20−30 min. After this, the electrodes were rinsed with DCB to remove excess uncoordinated zinc complex. Figure 1a shows pictures of the sensitizers in solution and upon surface modification. Corrected absorbances in the range 0.14−0.37 for the Soret bands of the sensitizers were obtained [Figure S2 in the Supporting Information (SI)]. When TiO_2 was modified with **5** lacking the axially coordinating ligand, some adsorption of the sensitizer occurred with optical density less than 0.05 (see Figure 1a). These results indicate effective immobilization via axial coordination of the zinc tetrapyrroles[4,5] in the case of TiO_2 surfaces modified with **1**−**4**.

Chart 1. Structures of the Nitrogenous Ligands Possessing Carboxylic Acids Used To Modify the TiO_2 Surface (**1**−**4**), the Sensitizers (**6** and **7**), and the Dyad (**8**) Used To Axially Coordinate the Immobilized Nitrogenous Bases on the TiO_2 Surface; **5** is a Control Compound Lacking the Axial Ligand Entity



Photoelectrochemical cells were constructed using platinized indium tin oxide as the counter electrode in noncoordinating DCB

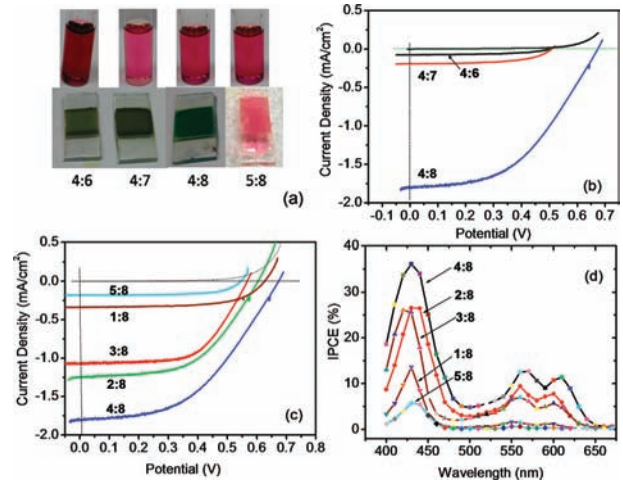


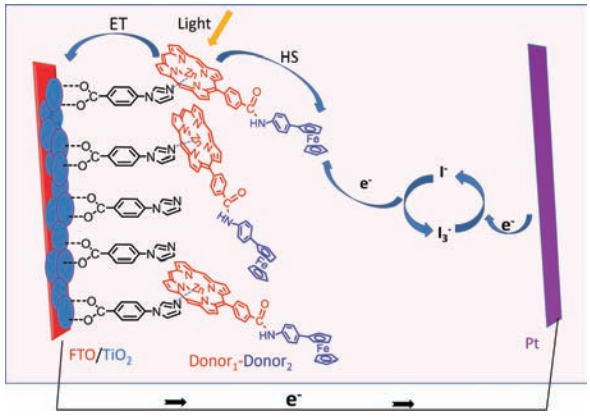
Figure 1. (a) Pictures of sensitizers in solution and on the FTO−TiO_2 electrodes modified with **4** or **5**. (b) $I-V$ characteristics showing the effect of different sensitizers bound to **4**-modified TiO_2. (c) $I-V$ characteristics showing the effect of different surface modifiers on the photoelectrochemical behavior upon binding of **8**. (d) IPCE curves for the electrodes used in (c). The $I-V$ curves were generated in DCB containing I_3^-/I^- (0.5 M/0.03 M) redox mediator using an AM 1.5 simulated light source with a 340 nm UV cutoff filter. The black lines in (b) and (c) are dark currents recorded for the **4**:**8**-modified electrode.

10.1021/ja9067113 CCC: $40.75

containing 0.5 M $(n\text{-Bu})_4$NI and 0.03 M I_2 as the redox mediator (see the SI for experimental details). We chose four nitrogenous bases with different pK_a values[6] to modify the TiO_2 surface, two zinc tetrapyrroles (**6** and **7**) having slightly different spectral and redox behaviors to demonstrate the versatility of the present method, and a zinc porphyrin−ferrocene (ZnP−Fc) $(donor)_1$−$(donor)_2$-type dyad (**8**) to exhibit improved photoelectrochemical behavior as a result of an electron transfer−hole migration mechanism.

Figure 1b shows typical $I-V$ plots for sensitizers bound to **4**-modified TiO_2. Similar-looking $I-V$ plots with lower photocurrents were obtained for electrodes modified with surface modifiers **1**−**3**. The photocurrents (I_{SC}) generated for **4**:**6**- and **4**:**7**-modified electrodes were nearly an order of magnitude smaller than that obtained for the dyad **4**:**8**-modified electrode. The photovoltages (V_{OC}) were also found to be smaller for the former electrodes. For the **4**:**8**-modified electrode, the V_{OC} and I_{SC} were found to be 0.67 V and 1.6 mA/cm^2, respectively. Furthermore, the performance of this dyad was tested for other surface modifiers. As shown in Figure 1c, higher currents were obtained for each of these electrodes than for those modified with simple sensitizers. For a given zinc tetrapyrrole, the $I-V$ performance for the various surface modifiers followed the order **4** > **2** > **3** > **1** > **5**, that is, it largely followed the metal−ligand binding constants of a given zinc tetrapyrrole.[6] The incident-photon-to-current efficiency (IPCE) plots for the electrodes used in Figure 1c are shown in Figure 1d. The shapes resembled those of the absorbance spectra of the sensitizers (see Figures S1 and S3 in the SI for the UV−vis spectra and IPCE curves, respectively, for the other sensitizer electrodes), suggesting that they are indeed responsible for the photovoltaic behavior. Additionally, photoswitching experiments revealed reproducible photocurrent generation (Figure S4 in the SI), indicating little or no dissociation of the coordinated sensitizer. The IPCEs at the Soret band locations were found to be 37, 28, 26, 14, and 6%, respectively, for the electrodes with **4**:**8**-, **2**:**8**-, **3**:**8**-, **1**:**8**-, and **5**:**8**-modified surfaces. For the **4**:**8**-modified photocell, the fill-factor and conversion efficiencies were found to be 47% and 0.56, respectively.

Scheme 1. Schematics of the Zinc Porphyrin−Ferrocene Dyad (**8**) Surface Modified via Axial Coordination of **4** Immobilized onto the TiO_2 Film on the FTO Electrode (the Photochemical and Redox Processes Are Shown by Arrows)



The photochemical events resulting in enhanced photocurrent in the case of the ZnP−Fc $(donor)_1$−$(donor)_2$ dyad-modified TiO_2 electrode are shown in Scheme 1. Excitation of the donor zinc porphyrin of the dyad results in injection of an electron into TiO_2, generating ZnP$^{\bullet+}$.[7] Because of favorable redox potentials,[8] a hole migration subsequently occurs, neutralizing ZnP$^{\bullet+}$ and resulting in the formation of Fc^+. The mediator I^- neutralizes Fc^+ to form I_3^-, which is subsequently reduced by the photoejected electron via the counter electrode, thus closing the circuit. The present electron transfer−hole migration mechanism[10] differs from the sequential electron transfer (from the photoexcited donor to the acceptor to the TiO_2) often observed in the case of donor−acceptor-modified electrodes,[2] signifying the importance of the present biomimetic approach for superior photovoltaic performance.

In summary, we have devised an elegant method of self-assembly for modification of a TiO_2 surface using coordinating ligands followed by immobilization of variety of sensitizers and a dyad. A maximum IPCE value of 37% was achieved for the TiO_2 electrode modified with **4**:**8**, a novel feature that is attributed to an electron transfer−hole migration mechanism of the dyad. Currently, utilization of this approach to modify nanocrystalline TiO_2 and other semiconductor surfaces using different $(donor)_1$−$(donor)_2$, donor−acceptor, and antenna-donor-type dyads and triads and evaluation of their photoelectrochemical performance and the kinetics of electron ejection and hole migration are in progress in our laboratory.

Acknowledgment. This work was financially supported by the National Science Foundation (Grant 0804015) and NSF-EPSCoR grants.

Supporting Information Available: Experimental details, UV−vis spectra of the investigated sensitizers in solution and on the TiO_2/FTO surface, IPCE curves, and light switching of photocurrent generation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Photoinduced electron transfer from ^{1}ZnP* to Fc in **8** occurs at a rate of 6.0×10^8 s^{-1} (see ref 9), suggesting that the electron injection from ^{1}ZnP* to TiO_2 is faster than this process.

(8) The first oxidation of ZnP in **8** is located at 0.31 V while that of Fc is located at 0.0 V vs Fc/Fc$^+$ in DCB (see ref 9).

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JA9067113